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(54) Fungicidal 2,6,6'-trimethylbenzophenones

Fungizide 2,6,6'-Trimethylbenzophenone

2,6,6'-Triméthylbenzophénones fongicides

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(56) References cited:
EP-A- 0 727 141

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EP 0 899 255 B1

Description

[0001] This invention relates to certain 2,6,6'-trimethylbenzophenone compounds, a novel process for their preparation, compositions containing such compounds, a method for combatting a fungus at a locus comprising treating the locus with such compounds and their use as fungicides.

[0002] Food production relies upon a variety of agricultural technologies to ensure the growing population's dietary needs remain affordable, nutritious and readily available on grocery store shelves. Fungicides are one of these agricultural technologies which are available to the world community. Fungicides are agrochemical compounds which protect crops and foods from fungus and fungal diseases. Crops and food are constantly threatened by a variety of fungal organisms, which, if left uncontrolled, can cause ruined crops and devastated harvests.

[0003] In particular, ascomycetes, the causative agent for powdery mildew diseases are an ever-present threat especially to cereal and fruit crops. However, applications of fungicidal agents at disease control rates can cause phytotoxic damage to the target plants.

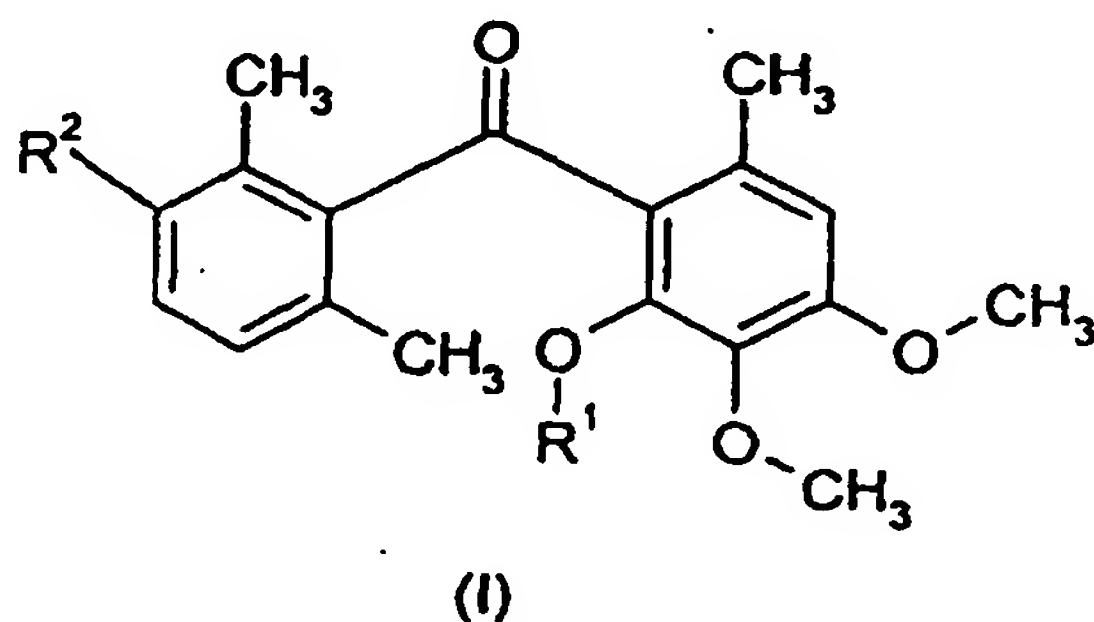
[0004] The compounds of the present invention are disclosed in a broad general formula of the European patent ("EP") application EP 0 727 141, which was published on August 21, 1996. The EP application discloses compounds having activity against phytopathogenic fungi, but relatively low systemicity.

[0005] There is no disclosure in the EP application of substituted benzophenones, wherein the first phenyl group is substituted by two methyl groups in the 2- and 6-position and an additional substituent in the 3-position.

[0006] Moreover, there is no hint given to a one-step process in which a methoxy group in the 2-position of the second phenyl group is directly replaced by an alkoxy group.

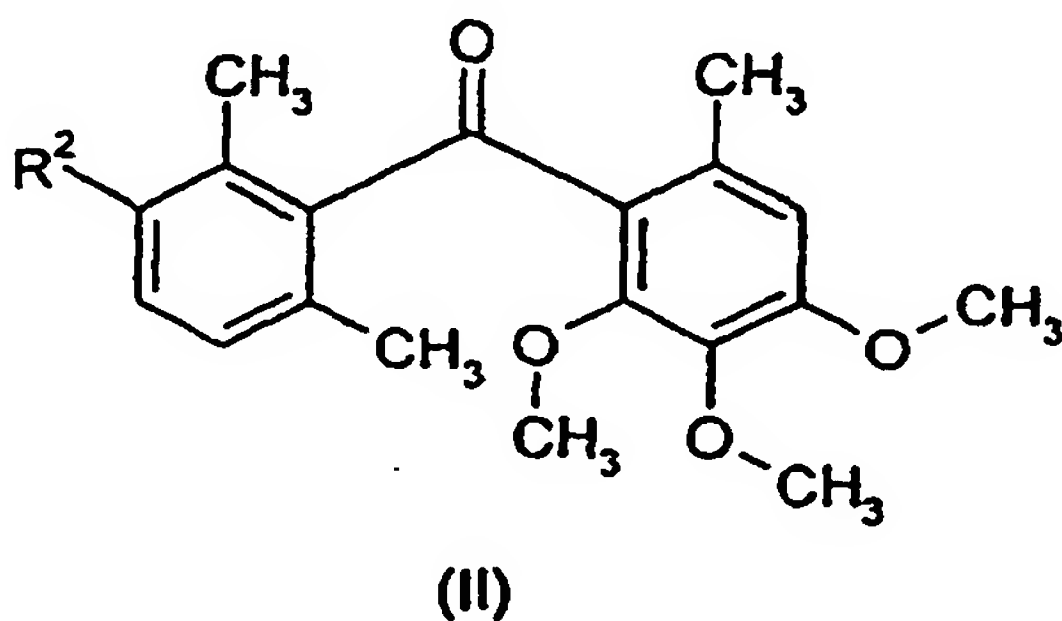
SUMMARY OF THE INVENTION

[0007] The present invention provides a process for the preparation of a compound of formula I,



in which

R¹ represents an optionally substituted C₂-C₆ alkyl, benzyl, cyclohexylmethyl or C₃-C₆ alkenyl group, and R² represents a hydrogen or a halogen atom, or an optionally substituted alkoxy group or a nitro group, which comprises reacting a compound of formula II,



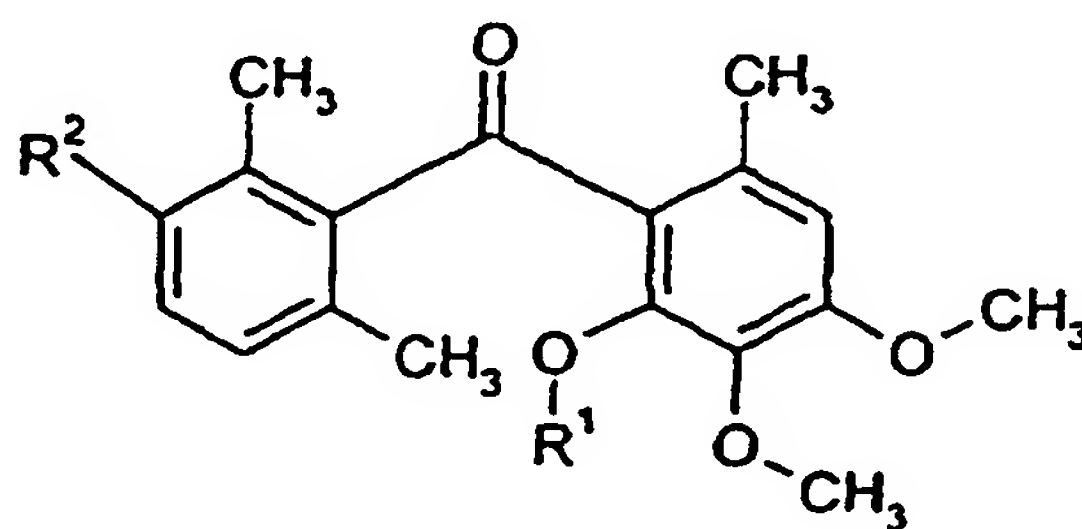
wherein R^2 has the meaning given, with a compound of formula III,



(III)

wherein R^1 has the meaning given and Met denotes an alkali metal atom.

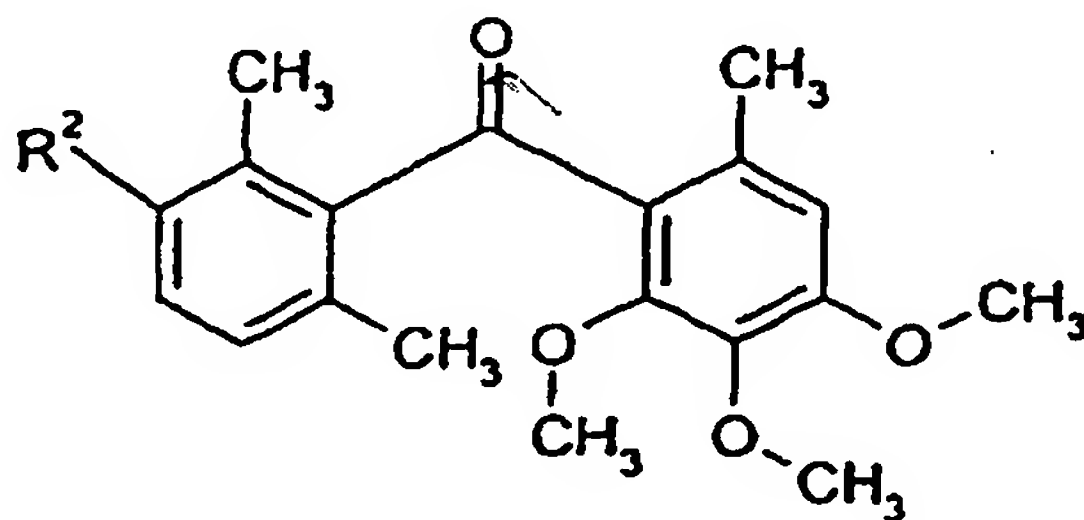
[0008] Moreover, the present invention relates to novel compounds of a compound of formula IA:



(IA)

wherein R^1 has the meaning given above, and R^2 represents a halogen atom, or an optionally substituted alkoxy group or a nitro group.

[0009] Furthermore, the present invention relates to novel compounds of formula IIA:



(IIA)

wherein R^2 represents a halogen atom, or an optionally substituted alkoxy group or a nitro group.

[0010] The compounds combine relatively excellent selective fungicidal activities in various crops with comparably high systemicities.

[0011] It is an object of the present invention to provide highly systemic fungicidal compounds.

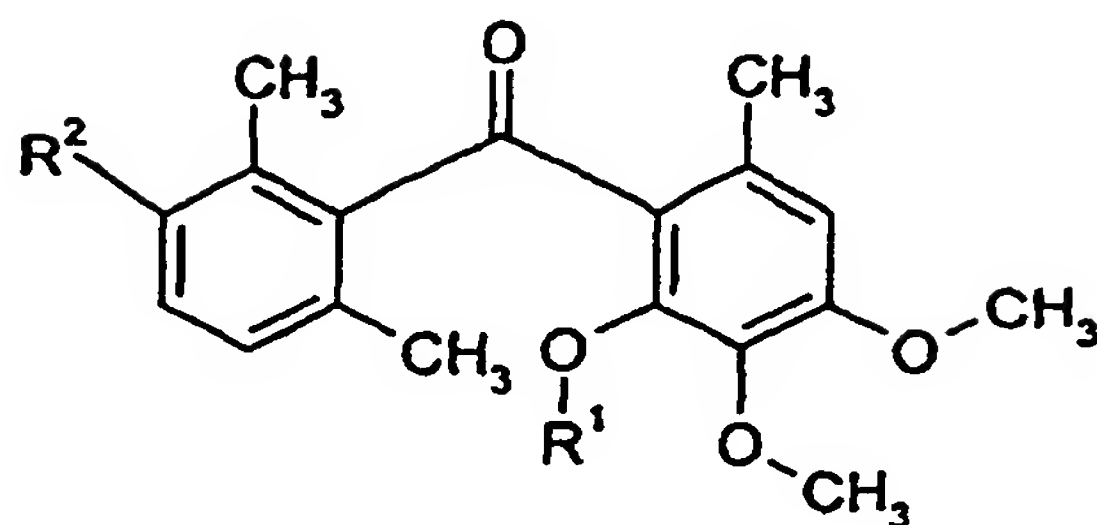
[0012] It is also an object of the invention to provide methods for controlling an undesired fungus by contacting said plants with a fungicidally effective amount of the compounds.

[0013] It is another object of the invention to provide selective fungicidal compositions containing the compounds as active ingredients.

[0014] These and other objects and features of the invention will be more apparent from the detailed description set forth hereinbelow, and from the appended claims.

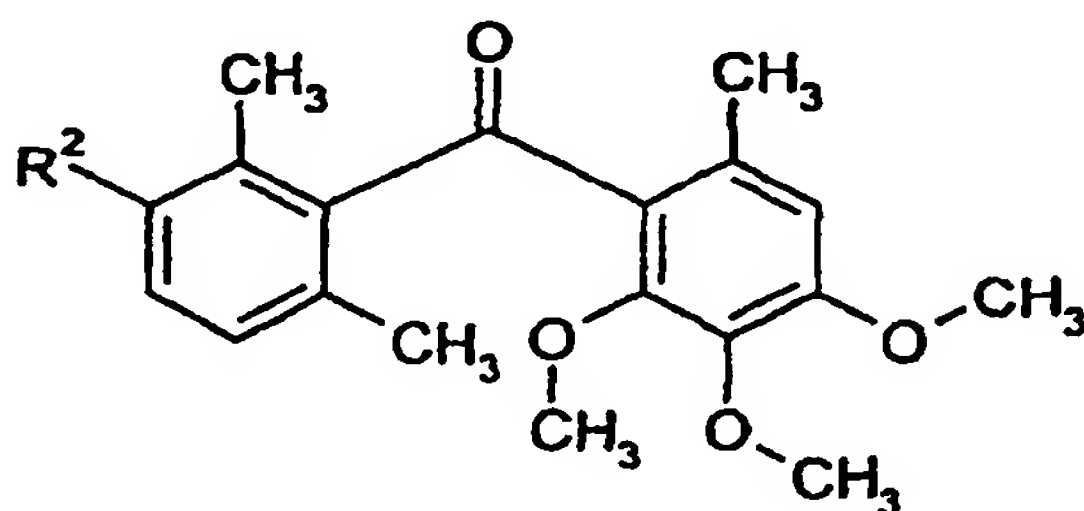
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] It has surprisingly been found that the compounds of formula I



(I)

can easily be prepared from compounds of formula II



(II)

by reaction with a compound of formula III



(III)

In which R¹, R², and Met have the meaning given above, in high yields. The R¹-O group selectively substitutes the methoxy group attached in the 2-position with respect to the benzoyl group without affecting the methoxy groups attached in the 3- and 4-position of the right-hand phenyl group. The compounds of formulae IA and IIA, which correspond to formulae I or II, but in which the radical R² is different from hydrogen, combine relatively excellent fungicidal activity against phytopathogenic fungi even at low dose rates, in particular those that cause powdery mildew diseases and have comparably high systemicity.

[0016] In general terms, unless otherwise stated, as used herein the term halogen atom may denote a bromine, iodine, chlorine or fluorine atom, and is especially a bromine, chlorine or fluorine atom.

[0017] Optionally substituted moieties may be unsubstituted or have from one up to the maximal possible number of substituents. Typically, 0 to 2 substituents are present. Each optionally substituted group independently is substituted by one or more halogen atoms or nitro, cyano, cycloalkyl, preferably C₃₋₆ cycloalkyl, cycloalkenyl, preferably C₃₋₆ cycloalkenyl, haloalkyl, preferably C₁₋₆ haloalkyl, halocycloalkyl, preferably C₃₋₆ halocycloalkyl, alkoxy, preferably C₁₋₆ alkoxy, haloalkoxy, preferably C₁₋₆ haloalkoxy, phenyl, mono- di- or trihalo-phenyl or pyridyl groups.

[0018] In general terms, unless otherwise stated herein, the terms alkyl, alkenyl and alkoxy as used herein with respect to a radical or moiety refer to a straight or branched chain radical or moiety. As a rule, such radicals have up to 10, in particular up to 6 carbon atoms. Suitably an alkyl or alkoxy moiety has from 1 to 6 carbon atoms, preferably from 1 to 5 carbon atoms. A preferred alkyl moiety is the methyl, ethyl, n-propyl, isopropyl or n-butyl group.

[0019] The invention especially relates to compounds of the general formulae IA and IIA in which any alkyl part of the groups R¹ and R², which may be straight chained or branched, contains 1 to 10 carbon atoms, preferably 1 to 9 carbon atoms, more preferably 1 to 6 carbon atoms, and in which each optionally substituted group independently is substituted by one or more halogen atoms or nitro, cyano, cycloalkyl, preferably C₃₋₆ cycloalkyl, cycloalkenyl, preferably C₃₋₆ cycloalkenyl, haloalkyl, preferably C₁₋₆ haloalkyl, halocycloalkyl, preferably C₃₋₆ halocycloalkyl, alkoxy, preferably C₁₋₆ alkoxy, haloalkoxy, preferably C₁₋₆ haloalkoxy, phenyl, or pyridyl groups, in which the phenyl moiety is optionally

substituted by one to three substituents selected from halogen atoms, cyano, C₁₋₆ alkyl and C₁₋₆ alkoxy groups.

[0020] The invention especially relates to compounds of the general formula IA in which R¹ represents a straight-chained or branched C₂₋₁₀ alkyl, in particular a straight-chained C₂₋₆ alkyl group, most preferably being an ethyl, n-propyl, n-butyl, n-pentyl group or a phenylmethyl group, in which the phenyl moiety may be unsubstituted or substituted by 1 to 5, preferably 1 to 3, substituents selected from the group consisting of halogen atoms, alkyl, alkoxy, haloalkyl and haloalkoxy groups.

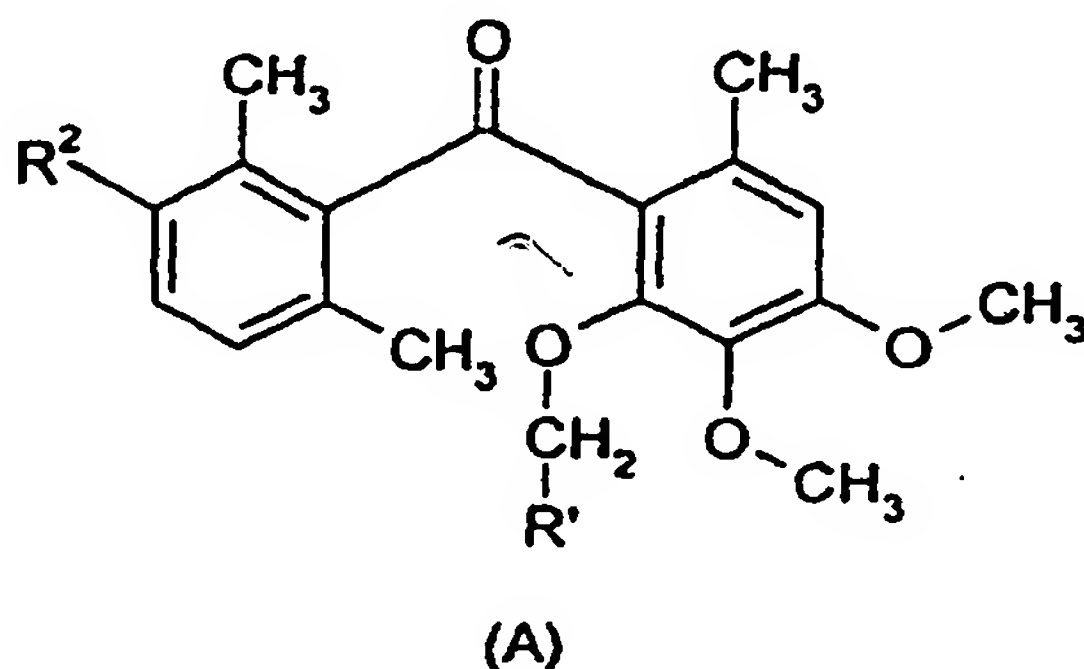
[0021] The invention especially relates to compounds of the general formulae IA and IIA in which R² represents a halogen atom, in particular a fluorine, chlorine, bromine or iodine atom, a nitro, a C₁₋₁₀ alkoxy or a C₁₋₁₀ haloalkoxy group, most preferred being a chlorine or bromine atom or a nitro or methoxy group.

[0022] The benzophenone compounds according to formulae IA and IIA are oils, gums, or, predominantly, crystalline solid materials and possess valuable fungicidal properties. For example, they can be used in agriculture, or related fields such as horticulture and viticulture, for the control of phytopathogenic fungi, especially ascomycetes, in particular powdery mildew diseases such as those caused by *Erysiphe graminis*, *Podosphaera leucotricha*, *Uncinula necator* and the like. Said benzophenone compounds possess a high fungicidal activity over a wide concentration range and may be used in agriculture without harmful phytotoxic effects.

[0023] Moreover, the compounds according to the invention show enhanced curative and residual control of fungi and fungal diseases such as cereal, cucumber and grape powdery mildew, and improved foliar systemicity compared with conventional fungicides.

[0024] Useful results in terms of control of phytopathogenic fungi are obtained with a compound as defined in formula IA and IIA, wherein R² represents a chloro or bromo atom or a methoxy or nitro group; R¹ in formula IA represents preferably an ethyl, n-propyl, butyl, n-pentyl group, or a benzyl group being optionally substituted by halogen;

[0025] In particular the compounds of formula A are preferred:



In which

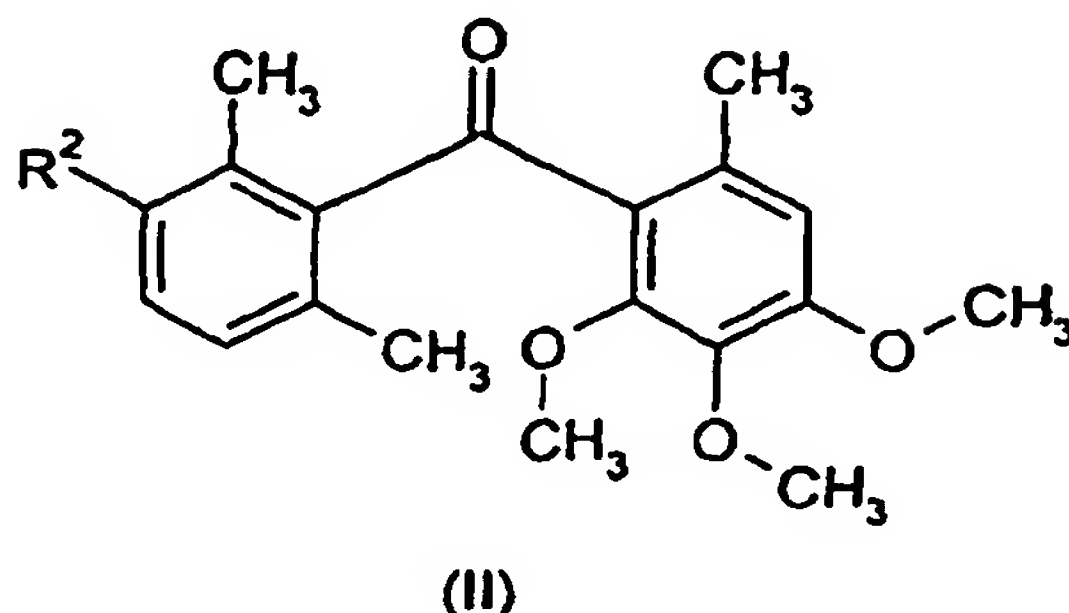
R² represents a chloro or bromo atom or a methoxy or nitro group, and R' represents a hydrogen atom or a C₁₋₅ alkyl or a phenyl group being optionally substituted by one or more fluorine or chlorine atoms or one or more C₁₋₄ alkyl groups.

[0026] Especially good results in terms of control of phytopathogenic fungi are obtained by using, for example, the following compounds of formula A:

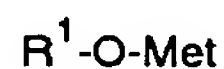
3-bromo-2'-butyloxy-3',4'-dimethoxy-2,6,6'-trimethylbenzophenone,
 2'-butyloxy-3-chloro-3',4'-dimethoxy-2,6,6'-trimethylbenzophenone,
 2'-butyloxy-3',4'-dimethoxy-3-nitro-2,6,6'-trimethylbenzophenone,
 2'-butyloxy-3,3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
 3-bromo-2'-benzyloxy-3',4'-dimethoxy-2,6,6'-trimethylbenzophenone,
 3-bromo-3',4'-dimethoxy-2'-(2-fluorobenzyloxy)-2,6,6'-trimethylbenzophenone,
 3-chloro-3',4'-dimethoxy-2'-(2-fluorobenzyloxy)-2,6,6'-trimethylbenzophenone,
 3',4'-dimethoxy-2'-(2-fluorobenzyloxy)-3-nitro-2,6,6'-trimethylbenzophenone,
 2'-(2-fluorobenzyloxy)-3,3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
 3-bromo-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
 3-chloro-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
 3-nitro-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
 2',3,3',4'-tetramethoxy-2,6,6'-trimethylbenzophenone.

[0027] The present invention further provides a process for the preparation of a compound of formula I, which com-

prises treating a compound of the general formula II:



wherein R² has the meaning given, with a compound of formula III,



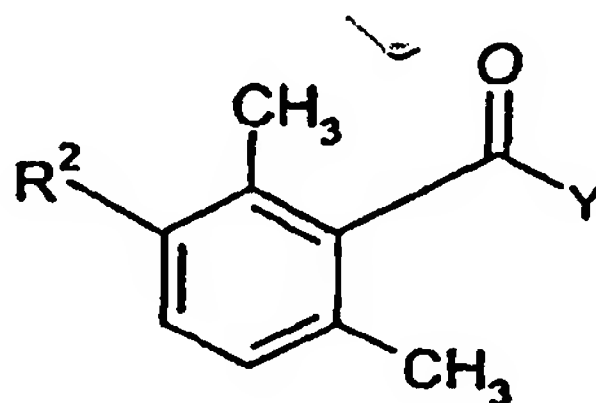
(III)

wherein R¹ has the meaning given and Met denotes an alkali metal atom.

[0028] The starting materials of formula II, wherein R² represents a hydrogen atom (e.g. EP 0 727 141), and III are known products, and may themselves be prepared according to established methods or routine adaptations thereof. Substituents which are not compatible with the selected reaction conditions may be introduced after formation of the benzophenone. They may be generated by known methods such as subsequent derivatization or substitution of a suitable group or by cleaving off a suitable protecting group.

[0029] The novel compounds of formula IIA preferably are prepared by a process which comprises

(a) reacting a compound of formula IV,



wherein R² has the meaning given above and Y represents a leaving group, in particular a chloro atom or a hydroxy group, with 3,4,5-trimethoxytoluene in the presence of a Lewis acid (Y= leaving group) or a dehydrating agent (Y = OH), preferably phosphorous pentoxide or POCl₃.

[0030] The reaction between the compounds of formula II and the compound of formula III is preferably carried out in the presence of a solvent, such as ethers like tetrahydrofuran, diethylether, *tert*-butyl-methylether or dimethoxyethane or an alcohol of formula R¹-OH or in mixtures of these solvents. The molar ratio between formula II and III is preferably in the range of 0.3 to 1.9 at a temperature between 25 and 150 °C.

[0031] As a rule an alcohol of formula R¹-OH is treated with a strong base, preferably an alkali metal such as sodium, an alkali metal hydride such as sodium hydride, an alkyllithium compound such as n-butyllithium or an alkali metal amide such as sodium amide. In a preferred embodiment the alcohol is treated with sodium hydride until the formation of hydrogen ceases. Subsequently, the compound of formula II or a mixture of the compound of formula II and an inert solvent, in particular dimethoxyethane, is added and the resulting reaction mixture heated to a temperature between 50 and 120 °C, in particular between 70 and 100 °C.

[0032] The compounds of formula II are preferably prepared by a Friedel Crafts reaction between the compound of formula IV and 3,4,5-trimethoxytoluene. The Friedel Crafts reaction is effected in the presence of a Lewis acid catalyst

according to well-established procedures ($Y = Cl$). Suitable catalysts include $FeCl_3$, $AlCl_3$, $SnCl_4$, $ZnCl_2$, $TiCl_4$, $SbCl_5$ and BF_3 , which may be in a molar equivalent amount (based on the benzoyl chloride of formula IV). However, it is also possible to use lesser amounts of catalyst at elevated temperatures, suitably under reflux temperatures, preferred catalysts under these conditions being $FeCl_3$, I_2 , $ZnCl_2$, iron, copper, strong sulphonic acids such as F_3CSO_3H , and acidic ion exchange resins such as Amberlyst® 15 and Nafion®. The preferred catalyst is $FeCl_3$ in a 0.001 to 0.2 molar ratio at a temperature of about 50 to 180°C. The reaction can be carried out in a solvent inert under the reaction conditions, for example ethylene or methylene chloride, benzene, octane, decane or solvent mixtures, or in the absence of solvent, conveniently by employing one of the reactants in excess, e.g. in the range of 1:5 to 5:1. If $AlCl_3$ is being used, the molar ratio is preferably in the range of 0.5 to 2 and the suitable solvents are e.g. methylenechloride or ethylenechloride at a temperature usually between -10 and 70°C.

[0033] The compounds of formula IV, wherein R^2 represents a halogen atom, are preferably prepared by a process which comprises the steps of:

- (a) reacting 2,6-dimethylbenzonitril with a halogenating agent in the presence of a Lewis acid, such as aluminium chloride; and
- (b) hydrolysing the resulting 3-halo-2,6-dimethylbenzonitril with a strong acid, such as sulfuric acid.

[0034] The compounds of formula IV, wherein R^2 represents a nitro group, are preferably prepared by treating 2,6-dimethylbenzoic acid with a mixture of sulfuric acid and nitric acid.

[0035] The compounds of formula IV, wherein R^2 represents an alkoxy group, are preferably prepared by a process which comprises the steps of:

- (a) reducing a compound of formula IV, wherein R^2 represents a nitro group;
- (b) treating the resulting 3-amino-2,6-dimethylbenzoic acid with aqueous sodium nitrite;
- (c) reacting the resulting 3-hydroxy-2,6-dimethylbenzoic acid with an alkylating agent of formula $R''-Y''$, in which R'' represents an alkyl group and Y'' represents a leaving group, in particular a halogen atom or a group of formula $-O-SO_2-OR''$, in which R'' has the meaning given.

[0036] The processes described below can analogously be applied to other starting compounds, if desired.

[0037] Due to excellent plant tolerance, the compounds of formulae IA and IIA may be used in cultivation of all plants where infection by the controlled fungi is not desired, e.g. cereals, vegetables, legumes, apples, vine. The absence of target crop phytotoxicity at fungus control rates is a feature of the present invention.

[0038] Accordingly the invention further provides a fungicidal composition which comprises a carrier and, as active ingredient, at least one compound of formula IA or IIA as defined above. A method of making such a composition is also provided which comprises bringing a compound of formula IA or IIA as defined above into association with at least one carrier. Such a composition may contain a single compound or a mixture of several compounds of the present invention. It is also envisaged that different isomers or mixtures of isomers may have different levels or spectra of activity and thus compositions may comprise individual isomers or mixtures of isomers.

[0039] A composition according to the invention preferably contains from 0.5% to 95% by weight of active ingredient

[0040] A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally gaseous but which has been compressed to form a liquid, and any of the carriers normally used in formulating fungicidal compositions may be used.

[0041] The compositions may be manufactured into e.g. emulsion concentrates, solutions which may be sprayed directly or diluted, diluted emulsions, wettable powders, soluble powders, dusts, granulates, water-dispersible granulates, microencapsulates by well-established procedures. The form of application such as spraying, atomizing, dispersing, pouring may be chosen like the compositions according to the desired objectives and the given circumstances.

[0042] The formulations, i.e. the compositions which comprise at least one compound according to general formula I and optionally solid and/or liquid auxiliaries and adjuvants, may be prepared by well-established procedures, e.g. intensive mixing and/or grinding of the active ingredients with other substances, such as fillers, solvents, solid carriers, and optionally surface-active compounds or adjuvants.

[0043] Solvents may be aromatic hydrocarbons, preferably the fractions C_6 to C_{12} , e.g. xylenes or xylene mixtures, substituted naphthalenes, phthalic acid esters, such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide, alkyl formamides, epoxidized vegetable oils, e.g. epoxidized coconut or soybean oil, water. Mixtures of different liquids are often suitable.

[0044] Solid carriers, which may be used for dusts or dispersible powders, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite, attapulgite. The physical properties may be improved by addition of highly dispersed silica gel or highly dispersed polymers. Carriers for granulates may be porous material, e.g. pumice, broken brick, sepiolite, bentonite, non-sorptive carriers may be calcite or sand. Additionally, a multitude of pre-granulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

[0045] Fungicidal compositions are often formulated and transported in concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surface-active agent facilitates this process of dilution. Thus, preferably one carrier in a composition according to the invention is a surface active agent. For example, the composition may contain at least two carriers, at least one of which is a surface active agent.

[0046] Suitable surface-active substances may be non-ionogenic, anionic or cationic surfactants with good dispersing, emulsifying and wetting properties depending on the nature of the compound according to general formula I to be formulated. Surfactants may also mean mixtures of surfactants.

[0047] Suitable surfactants may be so-called water-soluble soaps as well as water-soluble synthetic surface-active compounds.

[0048] Soaps usually are alkali, earth alkali or optionally-substituted ammonium salts of higher fatty acids (C_{10} - C_{20}), e.g. the sodium or potassium salts of oleic or stearic acid or of mixtures of natural fatty acids which are prepared, for example, from coconut or tallow oil. Furthermore, methyl-taurine salts of fatty acids may be used.

[0049] However, so-called synthetic surfactants are preferably used, especially fatty sulphonates, fatty sulphates, sulphonated benzimidazole derivatives or alkyl aryl sulphonates.

[0050] The fatty sulphates or fatty sulphonates are normally used as alkali, earth alkali or optionally-substituted ammonium salts and have an alkyl moiety of 8 to 22 carbon atoms, whereby alkyl also means the alkyl moiety of acyl residues, such as the sodium or calcium salt of lignin sulphonic acid, of sulphuric acid dodecylate or of a mixture of fatty alcohols prepared from natural fatty acids. This also includes the salts of sulphuric acid esters, sulphonic acids and adducts of fatty alcohols and ethylene oxide. The sulphonated benzimidazole derivatives preferably contain 2 sulphonic acid residues and a fatty acid residue with 8 to 22 carbon atoms. Alkyl aryl sulphonates are, for example, the sodium, calcium or triethyl ammonium salts of dodecyl benzene sulphonic acid, dibutyl naphthalene sulphonic acid or of a condensate of naphthalene sulphonic acid and formaldehyde.

[0051] Furthermore, phosphates, such as the salts of the phosphoric acid ester of a p-nonylphenol-(4-14)-ethylene oxide adduct or phospholipids, may be used.

[0052] Non-ionic surfactants are preferably polyglycolether derivatives of aliphatic or cycloaliphatic alcohols, saturated or non-saturated fatty acids and alkylphenols, which have 3 to 10 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon residue and 6 to 18 carbon atoms in the alkyl residue of the alkyl phenols.

[0053] Other suitable non-ionic surfactants are the water-soluble, 20 to 250 ethylene glycol ether groups containing polyadducts of ethylene oxide and polypropylene glycol, ethylene diamine polypropylene glycol and alkyl polypropylene glycol with 1 to 10 carbon atoms in the alkyl moiety, the substances normally contain 1 to 5 ethylene glycol units per propylene glycol unit.

[0054] Examples of non-ionic surfactants are nonylphenol polyethoxy ethanol, castor oil polyglycol ether, polyadducts of ethylene oxide and polypropylene, tributyl phenoxy polyethoxy ethanol, polyethylene glycol, octyl phenoxy polyethoxy ethanol.

[0055] Furthermore, fatty acid esters of polyoxy ethylene sorbitan, such as polyoxy ethylene sorbitan trioleate may be used.

[0056] Cationic surfactants preferably are quaternary ammonium salts, which have at least one alkyl residue with 8 to 22 carbon atoms and, furthermore, low, optionally-halogenated alkyl, benzyl or hydroxyalkyl residues. The salts are preferably halides, methyl sulphates or alkyl sulphates, e.g. stearyl trimethyl ammonium chloride or benzyl bis(2-chloroethyl) ethyl ammonium bromide.

[0057] The compositions of the invention may for example be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates emulsions, suspension concentrates and aerosols. Wettable powders usually contain 25%, 50% or 75% w/w of active ingredient and usually contain in addition to solid inert carrier, 3%-10% w/w of a dispersing agent and, where necessary, 0%-10% w/w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition usually containing 0.5%-10% w/w of active ingredient. Granules are usually prepared to have a size between 10 and 100 mesh ASTM (approx. 2.00 mm - 0.15 mm), and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain 0.5%-75% active ingredient and 0-10% w/w of additives such as stabiliser, surfactants, slow release modifiers and binding agents. The so called "dry flowable powders" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1%-50% w/v active ingredient, 2%-20% w/v emulsifiers and 0%-20% w/v of other additives

such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are usually compounded so as to obtain a stable, non-sedimenting flowable product and usually contain 10%-75% w/w active ingredient, 0.5%-15% w/w of dispersing agents, 0.1%-10% w/w of suspending agents such as protective colloids and thixotropic agents, 0%-10% of other additives such as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as antifreeze agents for water.

[0058] Aqueous dispersions and emulsions, for example compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonnaise' like consistency.

[0059] The composition of the invention may also contain other ingredients, for example other compounds possessing herbicidal, insecticidal or fungicidal properties.

[0060] Of particular interest in enhancing the duration of the protective activity of the compounds of this invention is the use of a carrier which will provide slow release of the fungicidal compounds into the environment of a plant which is to be protected. Such slow-release formulations could, for example, be inserted in the soil adjacent to the roots of a plant, or could include an adhesive component enabling them to be applied directly to the stem of a plant.

[0061] As commodity the compositions may preferably be in a concentrated form whereas the end-user generally employs diluted compositions. The compositions may be diluted to a concentration of 0.001% of active ingredient (a.i.). The doses usually are in the range from 0.01 to 10 kg a.i./ha.

[0062] The compositions of this invention can comprise also other compounds having biological activity, e.g. compounds having similar or complementary fungicidal activity or compounds having plant growth regulating, herbicidal or insecticidal activity.

[0063] The other fungicidal compound can be, for example, one which is capable of combating diseases of cereals (e.g. wheat) such as those caused by *Erysipha*, *Puccinia*, *Septoria*, *Gibberella* and *Helminthosporium* spp., seed and soil borne diseases and downy and powdery mildews on vines and powdery mildew and scab on apples etc. These mixtures of fungicides can have a broader spectrum of activity than the compound of general formula I alone. Furthermore, the other fungicide can have a synergistic effect on the fungicidal activities of the compound of general formula I.

[0064] Examples of the other fungicidal compounds are anilazine, azoxystrobin, benalaxyl, benomyl, binapacryl, bitertanol, biastocidin S, Bordeaux mixture, bromuconazole, bupirimate, captan, captan, carbendazim, carboxin, carpropamid, chlorbenzthiazon, chlorothalonil, chlozolinate, copper-containing compounds such as copper oxychloride, and copper sulfate, cycloheximide, cymoxanil, cypofuram, cyproconazole, cyprodinil, dichlofluanid, dichlorone, dichloran, diclobutrazol, diclomezine, dlethofencarb, difenoconazole, dimethirimol, dimethomorph, diniconazole, dinocap, ditalimfos, dithianon, dodemorph, dodine, edifenphos, epoxiconazole, etaconazole, ethirimol, etridiazole, famoxadone, fenapanil, fenarimol, fenbuconazole, fenfuram, fenpiclonil, fenpropidin, fenprolmorph, fentin, fentin acetate, fentin hydroxide, ferimzone, fluazlam, fludioxonil, flumetover, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminum, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, imazalil, iminoctadine, ipconazole, iprodione, isoprothioicane, kasugamycin, kitazin P, kresoxim-methyl, mancozeb, maneb, mepanipyrim, mepronil, metalaxyl, metconazole, methfuroxam, myclobutanil, neoasozin, nickel dimethyldithiocarbamate, nitrothallolpropyl, nuarimol, ofurace, organo mercury compounds, oxadixyl, oxycarboxin, penconazole, pencycuron, phenazineoxide, phthalide, polyoxin D, pyram, probenazole, prochloraz, procymidione, propamocarb, propiconazole, proplneb, pyrazophos, pyrifenoxy, pyrimethanil, pyroquilon, pyroxyfur, quinomethionate, quinoxifen, quintozone, spiroxamine, SSF-126, streptomycin, sulfur, tebuconazole, tecloftalame, tecnazene, tetraconazole, thlabendazole, thifluzamide, thiofanate-methyl, thiram, tolclofosmethyl, tolylfluanid, triadimefon, triadimenol, triazbutyl, tricyclazole, tridemorph, triflumizole, triforine, triticonazole, validamycin A, vinclozolin, XRD-563, zarilamid, zineb, ziram

[0065] In addition, the co-formulations according to the invention may contain at least one benzophenone of formula IA or IIA and any of the following classes of biological control agents such as viruses, bacteria, nematodes, fungi, and other microorganisms which are suitable to control insects, weeds or plant diseases or to induce host resistance in the plants. Examples of such biological control agents are: *Bacillus thuringiensis*, *Vedicillium lecanii*, *Autographica californica* NPV, *Beauveria bassiana*, *Ampelomyces quisqualis*, *Bacillus subtilis*, *Pseudomonas fluorescens*, *Streptomyces griseoviridis* and *Trichoderma harzianum*.

[0066] Moreover, the co-formulations according to the invention may contain at least one benzophenone of formula IA or IIA and a chemical agent that induces the systemic acquired resistance in plants such as for example nicotinic acid or derivatives thereof or BION.

[0067] The compounds of general formula can be mixed with soil, peat or other rooting media for the protection of the plants against seed-borne, soil-borne or foliar fungal diseases.

[0068] The invention still further provides the use as a fungicide of a compound of the general formula IA or IIA as defined above or a composition as defined above, and a method for combating fungus at a locus, which comprises treating the locus, which may be for example plants subject to or subjected to fungal attack, seeds of such plants or the medium in which such plants are growing or are to be grown, with such a compound or composition.

[0069] The present invention is of wide applicability in the protection of crop and ornamental plants against fungal attack. Typical crops which may be protected include vines, grain crops such as wheat and barley, rice, sugar beet, top fruit, peanuts, potatoes, vegetables and tomatoes. The duration of the protection is normally dependent on the individual compound selected, and also a variety of external factors, such as climate, whose impact is normally mitigated by the use of a suitable formulation.

[0070] The following examples further illustrate the present invention. It should be understood, however, that the invention is not limited solely to the particular examples given below.

Example 1

Preparation of 3-bromo-2,6,6'-trimethyl-2',3',4'-trimethoxy-benzophenone

1A 3-Bromo-2,6-dimethylbenzonitrile

[0071] A mixture of 2,6-dimethylbenzonitrile (5.0 g, 38.0 mmol), bromine (1.9 ml, 38.0 mmol) and chloroform (10 ml) is stirred at room temperature for 24 hours and subsequently heated to 60 °C for 6 hours. Upon cooling down to 0 °C, 10 g of AlCl₃ are added and the mixture is stirred for 4 hours at 0 °C. The reaction mixture is poured into water and extracted with toluene. The organic phase is separated and concentrated and the residue is purified by column chromatography yielding the pure product as brown crystals, 6.2 g, mp. 60 °C.

1B 3-Bromo-2,6-dimethylbenzoic acid

[0072] A mixture of 1A (6.0 g) and sulfuric acid (18.0 g, 80 %) is heated to 150 °C with stirring for 16 hours. The reaction mixture is diluted with ice-water and extracted with ethyl acetate. The organic phase is separated and concentrated and the residue is purified by column chromatography (petrol ether: ethyl acetate, 90:10 v/v) yielding the pure product as white crystals, 1.5 g, mp. 121 °C.

1C 5-Bromo-2,6,6'-trimethyl-2',3',4'-trimethoxy-benzophenone

[0073] A mixture of 1B (1.3 g, 5.7 mmol), 3,4,5-trimethoxytoluene (1.0 g; 5.7 mmol), P₂O₅ (3.5 g) and dichloromethane (20 ml) is stirred at room temperature for 16 hours. Subsequently, water (5 ml) and ice are added and dichloromethane is distilled off and the residue is extracted with toluene. The organic phase is washed with water and concentrated. The residue is recrystallized from petrol ethers/toluene. The solid material is collected by vacuum filtration, washed with cold petrol ethers and dried, yielding white crystals, 1.4 g, mp 859 °C.

Example 2

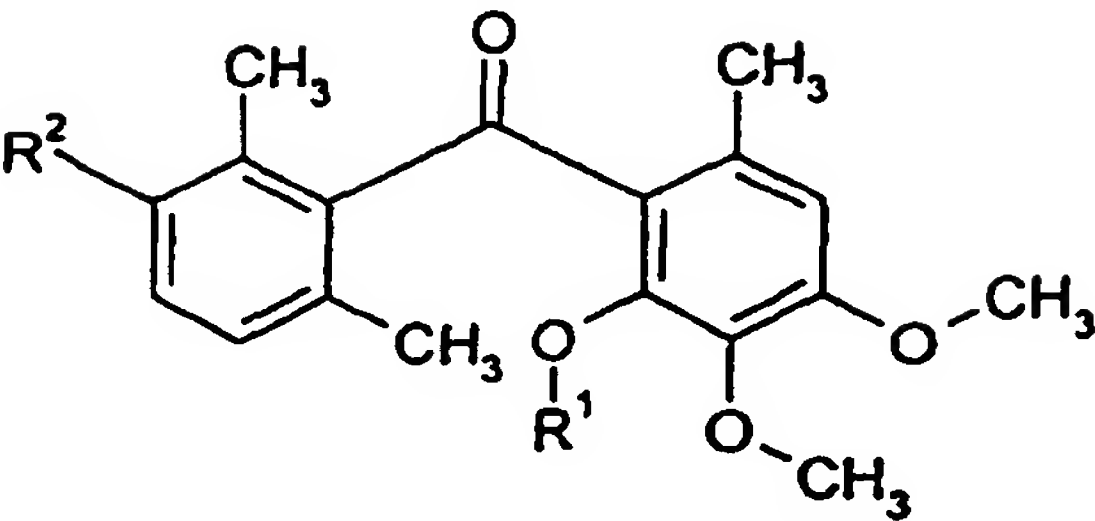
Preparation of 3-Bromo-2,6-dimethyl-2'-n-butoxy-3',4'-dimethoxybenzophenone

[0074] A mixture of n-butanol (5 ml) and sodium hydride (60 % in oil, 20 mmol) is stirred until the formation of H₂ gas ceases. A mixture of 1C (2.0 g, 5.0 mmol) and dimethoxyethane (15 ml) is added to the resulting reaction mixture. Subsequently, the reaction mixture is heated to 90 °C with stirring for 14 hours and dimethoxyethane is distilled off. A mixture of water and ethyl acetate (1:1 v/v; 100 ml) is then slowly added at room temperature. The organic phase is separated, concentrated and the residue is purified by column chromatography (petrol ether: ethyl acetate, 90:10 v/v) yielding the pure product as a yellow oil, 1.7 g (78.3 %).

Examples 3-49

[0075] Using essentially the same procedures described hereinabove for Examples 1 and 2 and employing standard derivatization techniques where appropriate, the following compounds are prepared and shown in Table I:

Table I



Example	R ¹	R ²	Melting point (° C)
3	CH ₃	NO ₂	138
4	CH ₃	CH ₃ O	95
5	CH ₃	Cl	oil
6	n-C ₅ H ₁₁	Br	oil
7	n-C ₃ H ₇	Br	oil
8	benzyl	Br	oil
9	C ₂ H ₅	Br	oil
10	pentafluorobenzyl	H	132
11	cyclohexylmethyl	H	52
12	benzyl	H	76
13	2,4,6-trifluorobenzyl	H	106
14	2,3,6-trifluorobenzyl	H	87
15	2,4,5-trifluorobenzyl	H	155
16	2,3,5-trifluorobenzyl	H	86

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17	3,5-difluorobenzyl	H	83
18	3,4-difluorobenzyl	H	96
19	2,5-difluorobenzyl	H	142
20	2,3-difluorobenzyl	H	79
21	2,4-difluorobenzyl	H	83-84
22	2,6-difluorobenzyl	H	110
23	3-fluorobenzyl	H	65-69
24	2-fluorobenzyl	H	90-91
25	4-fluorobenzyl	H	93-94
26	2,6-dichlorobenzyl	H	114-116
27	3,4-dichlorobenzyl	H	105-106
28	2,4-dichlorobenzyl	H	124-126
29	3-chlorobenzyl	H	103-104
30	2-chlorobenzyl	H	108-110
31	4-chlorobenzyl	H	102-105
32	3-chloro-2-fluorobenzyl	H	92
33	2-chloro-6-fluorobenzyl	H	118-120
34	3-methylbenzyl	H	74
35	3-methylbenzyl	H	83-85
36	4-methylbenzyl	H	104-105
37	3-methoxybenzyl	H	62-64
38	4-methoxybenzyl	H	99-101
39	4- <i>tert</i> -butylbenzyl	H	88-90
40	2,4-dimethylbenzyl	H	96-99
41	2,5-dimethylbenzyl	H	oil
42	4-trifluoromethylbenzyl	H	112-113
43	3-trifluoromethylbenzyl	H	119-121
44	4-bromobenzyl	H	106-108
45	3-bromobenzyl	H	122-123
46	2-bromobenzyl	H	10/-108

18-0

47	3-methylbutyl	H	81
48	n-butyl	H	75
49	n-pentyl	H	oil

10 Comparison experiment

Preparation of 3-Bromo-2,6-dimethyl-2'-n-butoxy-3',4'-dimethoxybenzophenone analogously to the method disclosed in EP 0727141

15 C-1 3-Bromo-2,6,6'-trimethyl-2'-hydroxy-3',4'-dimethoxy-benzophenone

[0076] Aluminium chloride (1.25 g, 10 mmol) is added to a mixture of 5-bromo-2,6,6'-trimethyl-2',3',4'-trimethoxybenzophenone obtained according to Example 1C (1.90 g, 4.7 mmol) and dichloromethane (5 ml). The mixture is stirred for 30 minutes at 0 °C and for 3 hours at ambient temperature. Subsequently the reaction mixture is poured into a mixture of ice and concentrated hydrochloric acid. The organic phase is separated and washed with dilute hydrochloric acid and water. The organic phase is dried and concentrated. The residue is purified by column chromatography (petrol ether : ethyl acetate, 95:5 v/v) yielding the pure product as yellow crystals, 1.2 g (67 %).

25 C-2 3-Bromo-2,6-dimethyl-2'-n-butoxy-3',4'-dimethoxybenzophenone

[0077] Potassium tert-butyrate (0.55 g, 5 mmol) is added to a mixture of C-1 (1.90 g, 5 mmol) and dimethylformamide (4 ml). Upon stirring for 15 minutes at ambient temperature n-butybromide (0.7 g, 5 mmol) is added to the reaction mixture. The mixture is stirred at ambient temperature for 14 hours and subsequently poured into water. The aqueous phase is extracted with toluene. The combined organic phases are washed with dilute potassium hydroxide, and water. The organic phase is dried and concentrated. The residue is purified by column chromatography (toluene) yielding the pure product as a yellow oil, 1.3 g (73 %). The overall yield starting from 1C in two steps was 49 % compared with 78.3 % obtained in one step with the process according to the invention (Example 2).

35 Biological Investigations

B Comparison of the curative and residual fungicidal activity of the 3-substituted -2,6,6'-trimethylbenzophenones with a corresponding benzophenone unsubstituted in the 3-position

40 Test diseases:

[0078]

(a) Wheat Powdery Mildew (WPM):

45 HOST: Wheat (*Triticum aestivum* L.) variety Kanzler
PATHOGEN: *Erysiphe graminis* DC. f.sp. *tritici* E. Marchal

(b) Cucumber Powdery Mildew (QPM):

50 HOST: Cucumber (*Cucumis sativus* L.) variety Bush pickle
PATHOGEN: *Erysiphe cichoracearum* DC

[0079] This test procedure is for curative and residual control of powdery mildew diseases.

- 55 1. Wheat seed (approximately 8-10/pot) or cucumber seed (1 seed /pot) is planted in 6 cm diameter plastic pots and maintained in the greenhouse.
2. When the primary leaf (wheat) or the cotyledons (cucumber) is/are fully expanded, formulated test compounds are sprayed with a single nozzle overhead track sprayer at a rate of 200 l/ha. Plants are then allowed to air-dry.

3. Inoculation precedes treatment by 2 days in the case of curative evaluations and follows treatment by 3 days in case of residual evaluations. For inoculation, plants are set up on greenhouse benches with bottom watering mats and inoculated by dusting them with conidia from powdery mildew infected plants (stock cultures at an age of 10-14 days). Between inoculation and treatment for curative evaluations and between treatment and inoculation for residual evaluations, plants are maintained in the greenhouse with bottom watering.

4. Disease on the primary leaf (wheat) or on the cotyledons (cucumber) as percent leaf area with disease symptoms/signs is evaluated about 7 days after inoculation. In the case of wheat, the tips and bases of the leaves are excluded from the evaluation.

Percent disease control is then calculated by the following formula:

$$\% \text{ disease control} = 100 - \frac{\% \text{ Infection in treated plants}}{\% \text{ infection in untreated plants}} \times 100$$

FORMULATION, REFERENCE COMPOUNDS AND CONTROLS:

[0080]

1. Technical compounds are formulated in a solvent/surfactant system consisting of 5% acetone and 0.05% Tween 20 in deionized water. Compounds are dissolved in acetone prior to addition of the water; the Tween 20 can be added through either the acetone or the water. Dilutions are made using the solvent/surfactant system. Formulated compounds are prepared using deionized water.

2. Two kinds of controls are included:

Plants treated with the solvent/surfactant solution and inoculated (Solvent Blank).
Untreated plants which are inoculated (Inoculated Control).

[0081] The results of this evaluation are shown in Table II:

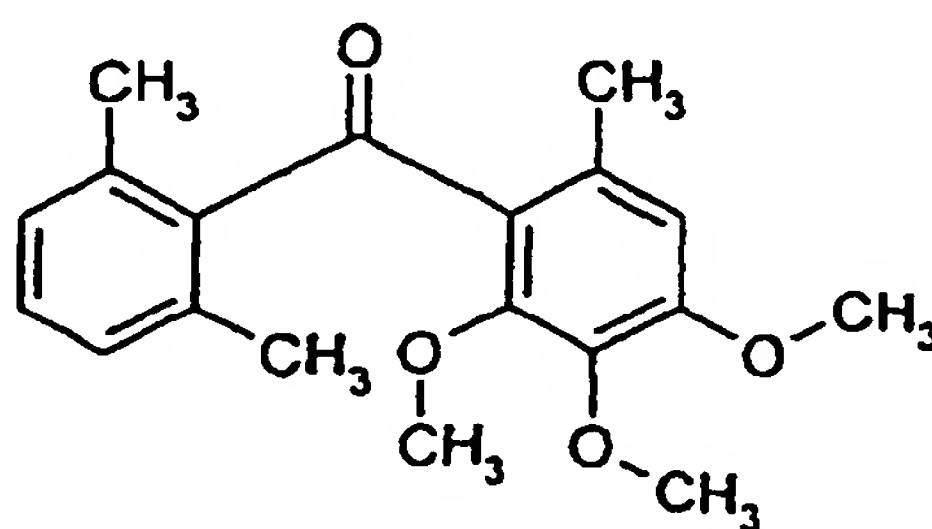
Table II Curative and Residual Fungicidal activity of 2,6,6'-trimethylbenzophenones

		WPM 2 da Curative	WPM 3 da Residual	QPM 3 da Residual
Example No.	a.i. [ppm]			
2	1250	92	100	100
	125	90	100	89
	12.5	87	100	0
3	1250	99	100	92
	125	96	100	2
	12.5	79	99	1
4	1250	94	100	98
	125	86	100	13
	12.5	73	100	0
5	1250	96	100	100
	125	93	100	66
	12.5	83	100	11
standard	1250	92	100	89
	125	74	81	6
	12.5	55	70	14

In curative applications, application follows inoculation.

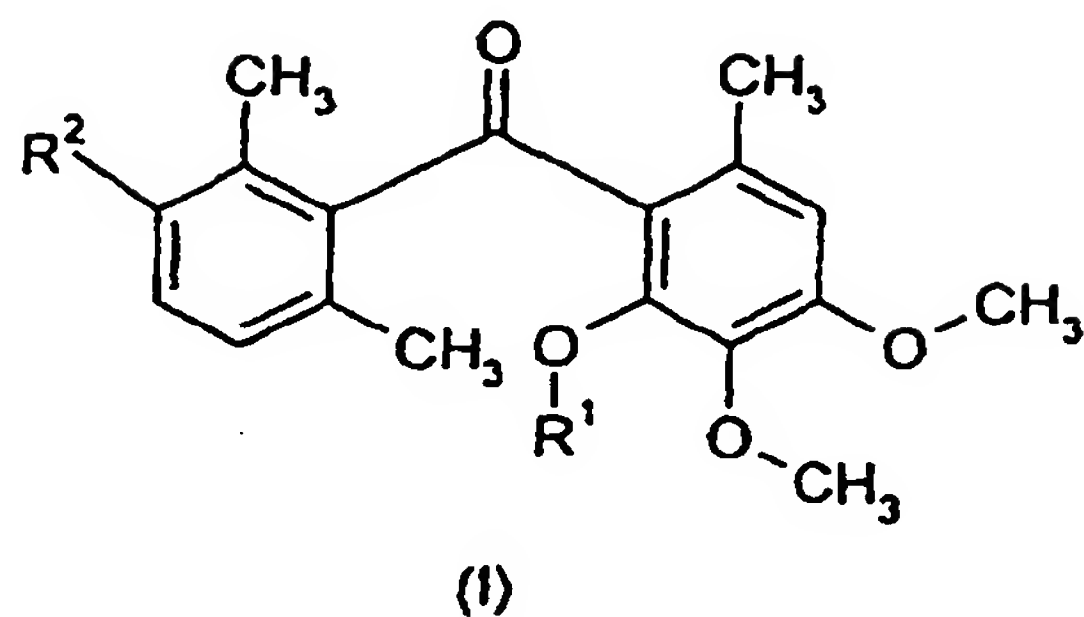
In residual applications, application precedes inoculation.

[0082] The following compound which is known from EP 0 727 141 has been used as standard:



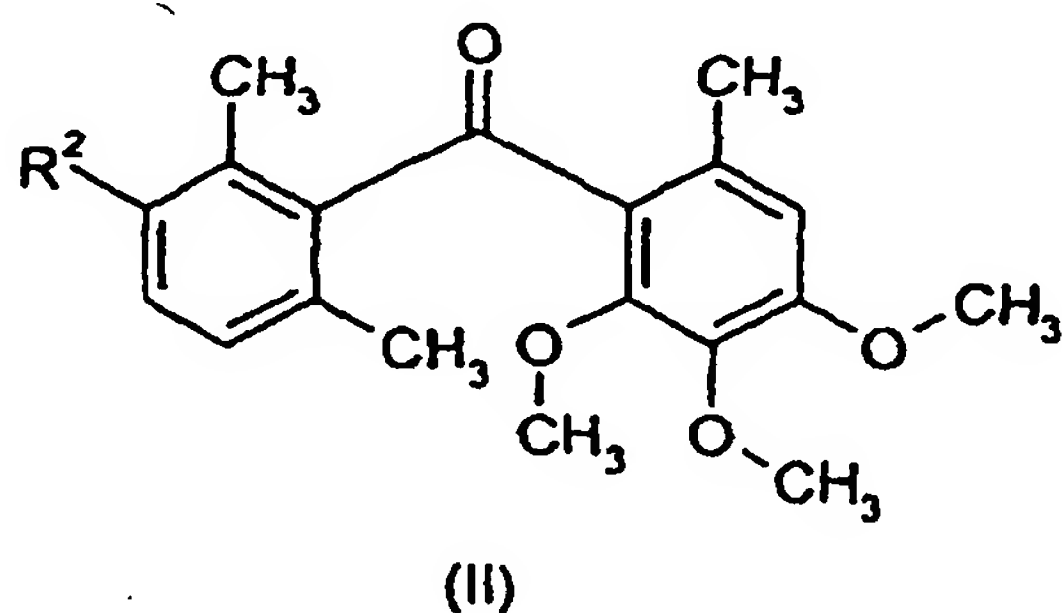
Claims

1. A process for the preparation of a compound of formula I,



15 in which

R^1 represents an optionally substituted C_2 - C_6 alkyl, benzyl, cyclohexylmethyl or C_3 - C_6 alkenyl group, and R^2 represents a hydrogen or a halogen atom, or an optionally substituted alkoxy group or a nitro group, which comprises reacting a compound of formula II,

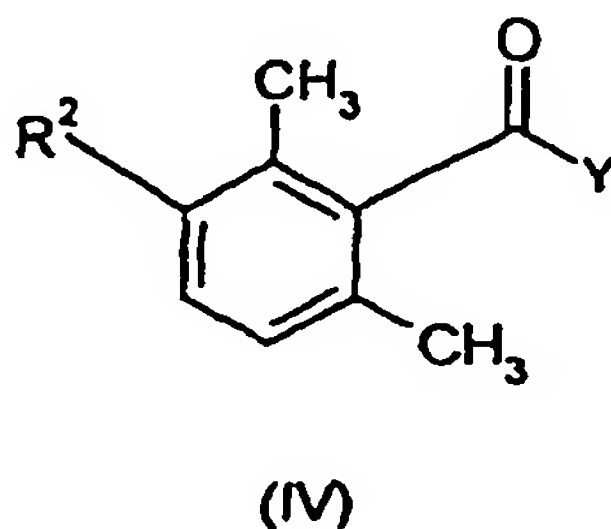


with a compound of formula III,



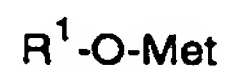
wherein R^1 and R^2 have the meaning as described above, and Met denotes an alkali metal atom.

- 40 2. A process for the preparation of a compound of formula I as described in claim 1, which comprises the steps of
- (a) reacting a compound of formula IV,



wherein R^2 is described in claim 1, and Y represents a halogen atom or a hydroxy group, with 3,4,5-trimethoxytoluene in the presence of a Lewis acid or phosphorus pentoxide; and

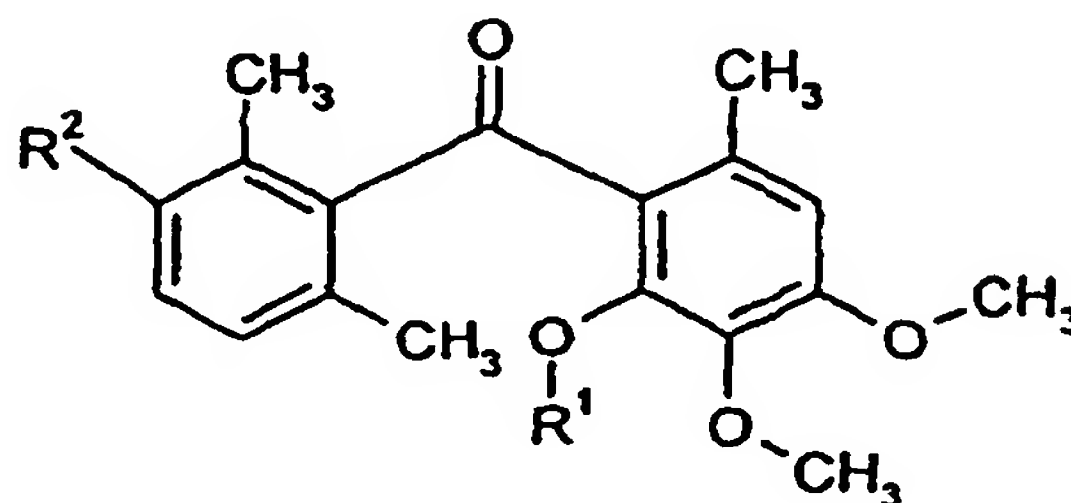
(b) treating the resulting benzophenone with a compound of formula III,



(III)

wherein R^1 is as described in claim 1 and Met denotes an alkali metal atom.

3. A compound of formula IA:



(IA)

wherein

R^1 represents an optionally substituted C_2-C_6 alkyl, benzyl, cyclohexylmethyl or C_3-C_6 alkenyl group, and R^2 represents a halogen atom, or an optionally substituted alkoxy group or a nitro group.

4. The compound of claim 3, wherein

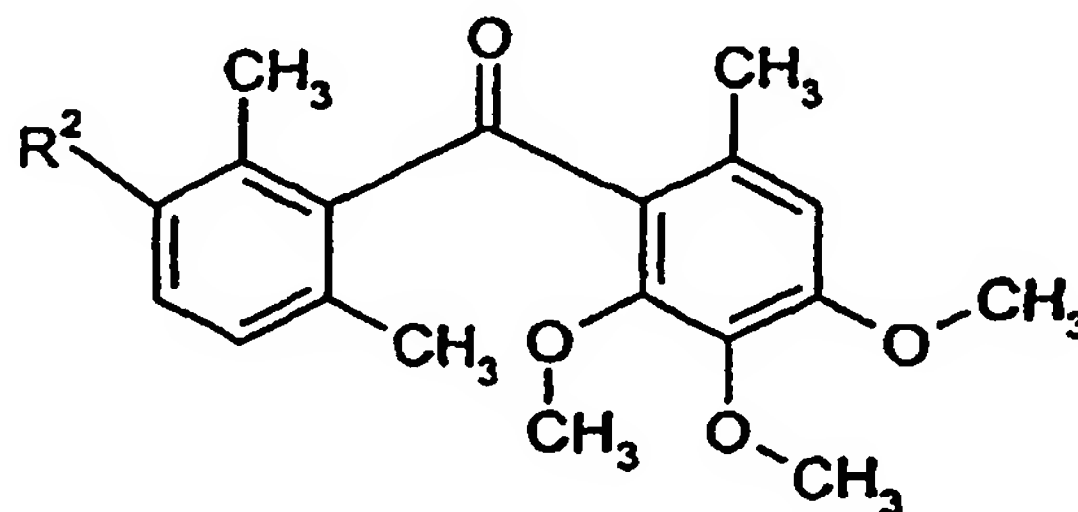
R^1 represents a C_{2-5} alkyl or benzyl group, being optionally substituted by one or two halogen atoms or a C_1-C_3 alkyl group;

R^2 represents a chloro or bromo atom, or a methoxy or a nitro group.

5. A compound as claimed in claim 4 being selected from the group consisting of

3-bromo-2'-butyloxy-3',4'-dimethoxy-2,6,6'-trimethylbenzophenone,
2'-butyloxy-3-chloro-3',4'-dimethoxy-2,6,6'-trimethylbenzophenone,
2'-butyloxy-3',4'-dimethoxy-3-nitro-2,6,6'-trimethylbenzophenone,
2'-butyloxy-3,3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
3-bromo-3',4'-dimethoxy-2'-(2-fluorobenzyloxy)-2,6,6'-trimethylbenzophenone,
3-chloro-3',4'-dimethoxy-2'-(2-fluorobenzyloxy)-2,6,6'-trimethylbenzophenone,
3',4'-dimethoxy-2'-(2-fluorobenzyloxy)-3-nitro-2,6,6'-trimethylbenzophenone,
2'-(2-fluorobenzyloxy)-3,3',4'-trimethoxy-2,6,6'-trimethylbenzophenone.

6. A compound of formula IIA:



(IIA)

wherein

R^2 represents a halogen atom, or an optionally substituted alkoxy group or a nitro group.

7. A compound as claimed in claim 6, wherein R^2 represents a chloro or bromo atom or a methoxy or a nitro group.

8. A compound as claimed in claim 7 being selected from the group consisting of
3-bromo-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
3-chloro-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenone,
3-nitro-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenone, and
2',3,3',4'-tetramethoxy-2,6,6'-trimethylbenzophenone.

9. A composition which comprises a fungicidally effective amount of at least one compound of Claim 3 or Claim 6 and a carrier.

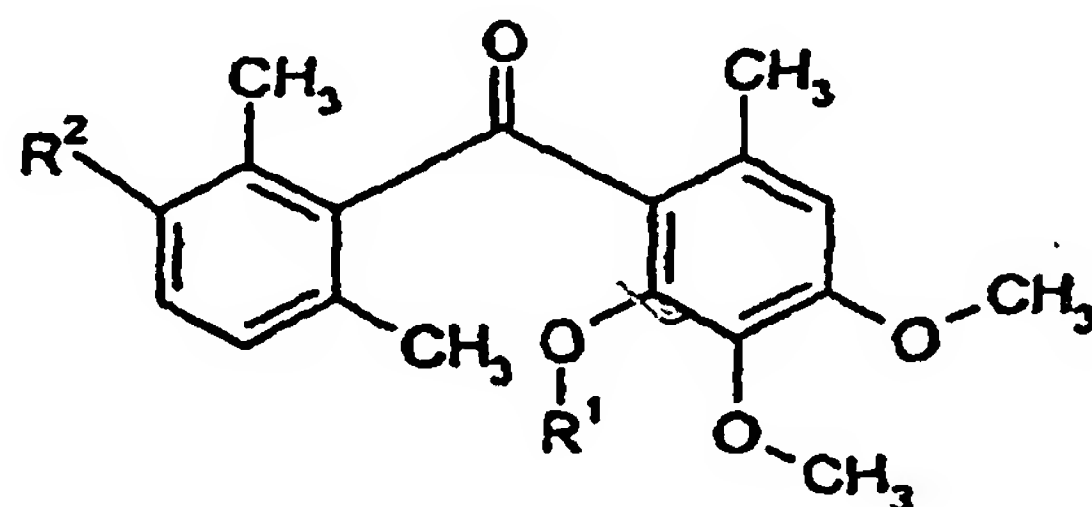
10. A method of combating fungus at a locus which comprises treating the locus with a compound of Claim 3 or Claim 6 or a composition of Claim 9.

11. The method according to Claim 10 wherein the disease is caused by ascomycetes.

12. The method according to Claim 10 wherein the fungus is a member of the taxonomic order Erysiphales.

Patentansprüche

1. Verfahren zur Herstellung von Verbindungen der Formel I

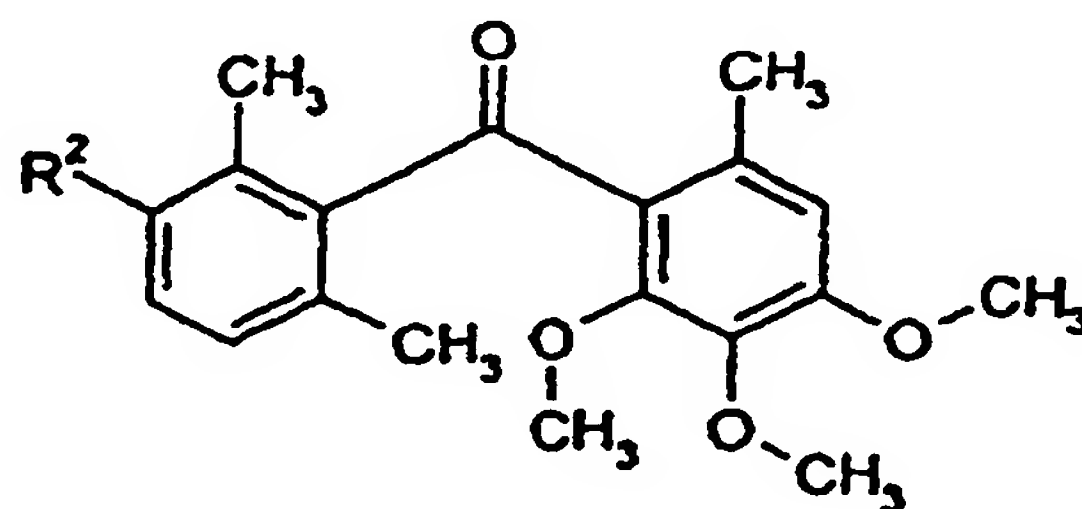


(I)

In welcher

R^1 für eine gegebenenfalls substituierte C_2 - C_6 -Alkyl-, Benzyl-, Cyclohexylmethyl- oder C_3 - C_6 -Alkenylgruppe steht und

R^2 für ein Wasserstoff- oder ein Halogenatom oder eine gegebenenfalls substituierte Alkoxygruppe oder eine Nitrogruppe steht, bei dem man eine Verbindung der Formel II



(II)

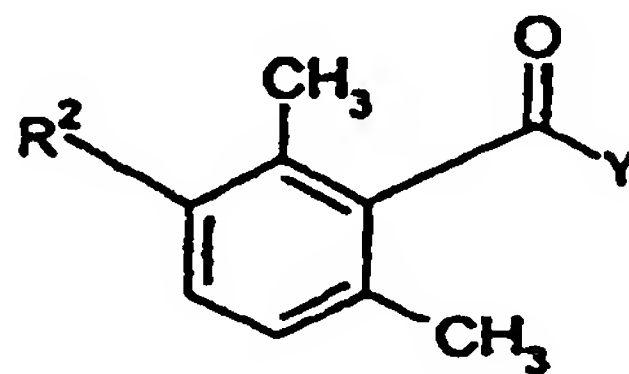
mit einer Verbindung der Formel III



wobei R^1 und R^2 die oben beschriebene Bedeutung haben und Met für ein Alkalimetallatom steht, umgesetzt.

2. Verfahren zur Herstellung einer Verbindung der Formel I nach Anspruch 1, bei dem man

(a) eine Verbindung der Formel IV



(IV)

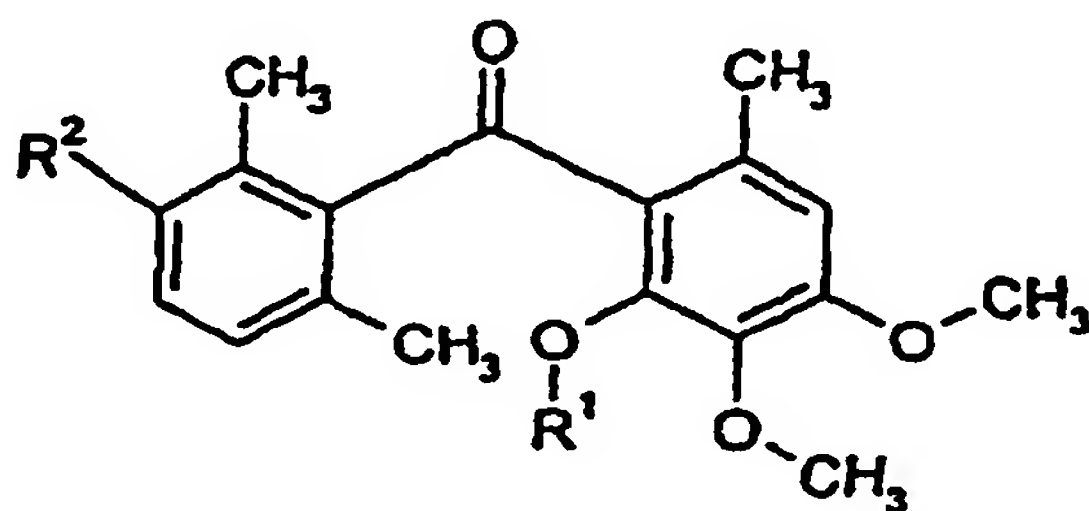
wobei R^2 wie in Anspruch 1 beschrieben ist und Y für ein Halogenatom oder eine Hydroxygruppe steht, in Gegenwart einer Lewisäure oder Phosphorpentoxid mit 3,4,5-Trimethoxytoluol umgesetzt; und

(b) das so erhaltene Benzophenon mit einer Verbindung der Formel III



wobei R^1 wie in Anspruch 1 beschrieben ist und Met für ein Alkalimetallatom steht, umgesetzt.

3. Verbindungen der Formel IA:



(IA)

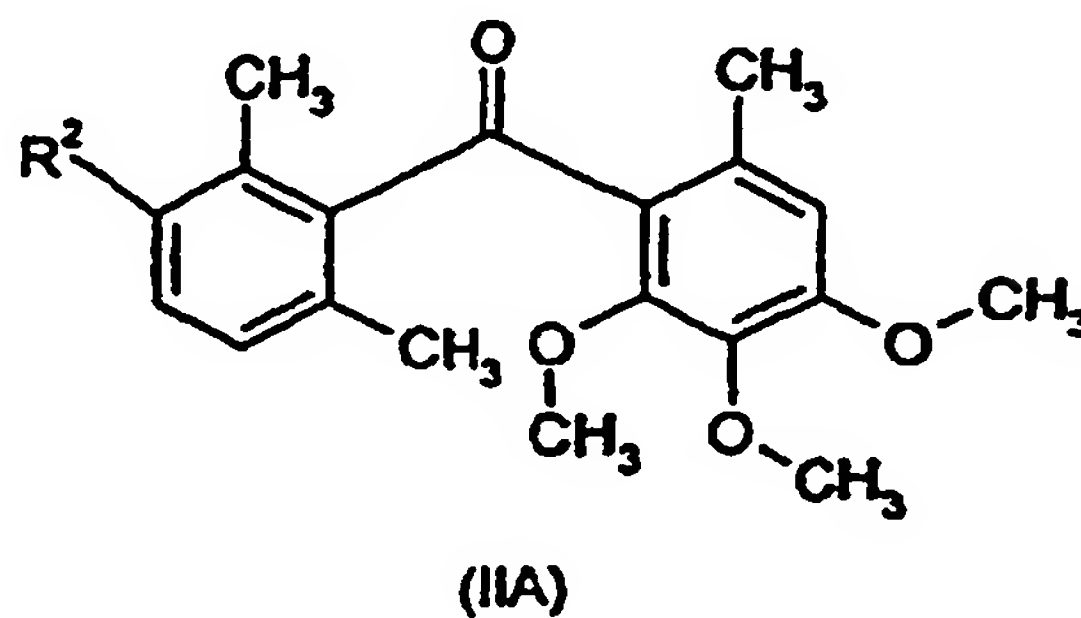
wobei R^1 für eine gegebenenfalls substituierte C_2 - C_6 -Alkyl-, Benzyl-, Cyclohexylmethyl- oder C_3 - C_6 -Alkenylgruppe steht, und R^2 für ein Halogenatom oder eine gegebenenfalls substituierte Alkoxygruppe oder eine Nitrogruppe steht.

4. Verbindungen nach Anspruch 3, wobei R^1 für eine C_2 - C_5 -Alkyl- oder Benzylgruppe steht, die gegebenenfalls durch ein oder zwei Halogenatome oder eine C_1 - C_3 -Alkylgruppe substituiert ist;

R² für ein Chlor- oder Bromatom oder eine Methoxy- oder eine Nitrogruppe steht.

5. Verbindungen nach Anspruch 4, ausgewählt aus der aus
 3-Brom-2'-butyloxy-3',4'-dimethoxy-2,6,6'-trimethylbenzophenon,
 2'-Butyloxy-3-chlor-3',4'-dimethoxy-2,6,6'-trimethylbenzophenon,
 2'-Butyloxy-3',4'-dimethoxy-3-nitro-2,6,6'-trimethylbenzophenon,
 2'-Butyloxy-3,3',4'-trimethoxy-2,6,6'-trimethylbenzophenon,
 3-Brom-3',4'-dimethoxy-2'-(2-fluorbenzyloxy)-2,6,6'-trimethylbenzophenon,
 3-Chlor-3',4'-dimethoxy-2'-(2-fluorbenzyloxy)-2,6,6'-trimethylbenzophenon,
 3',4'-Dimethoxy-2'-(2-fluorbenzyloxy)-3-nitro-2,6,6'-trimethylbenzophenon,
 2'-(2-Fluorbenzyloxy)-3,3',4'-trimethoxy-2,6,6'-trimethylbenzophenon
 bestehenden Gruppe.

6. Verbindungen der Formel IIA:



wobei

R² für ein Halogenatom oder eine gegebenenfalls substituierte Alkoxygruppe oder eine Nitrogruppe steht.

7. Verbindungen nach Anspruch 6, wobei
 R² für ein Chlor- oder Bromatom oder eine Methoxy- oder eine Nitrogruppe steht.

8. Verbindungen nach Anspruch 7, ausgewählt aus der aus
 3-Brom-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenon, 3-Chlor-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenon,
 3-Nitro-2',3',4'-trimethoxy-2,6,6'-trimethylbenzophenon und 2',3,3',4'-Tetramethoxy-2,6,6'-trimethylbenzophenon
 bestehenden Gruppe.

9. Zusammensetzung, enthaltend eine fungizid wirksame Menge von wenigstens einer Verbindung nach Anspruch 3 oder Anspruch 6 und einen Trägerstoff.

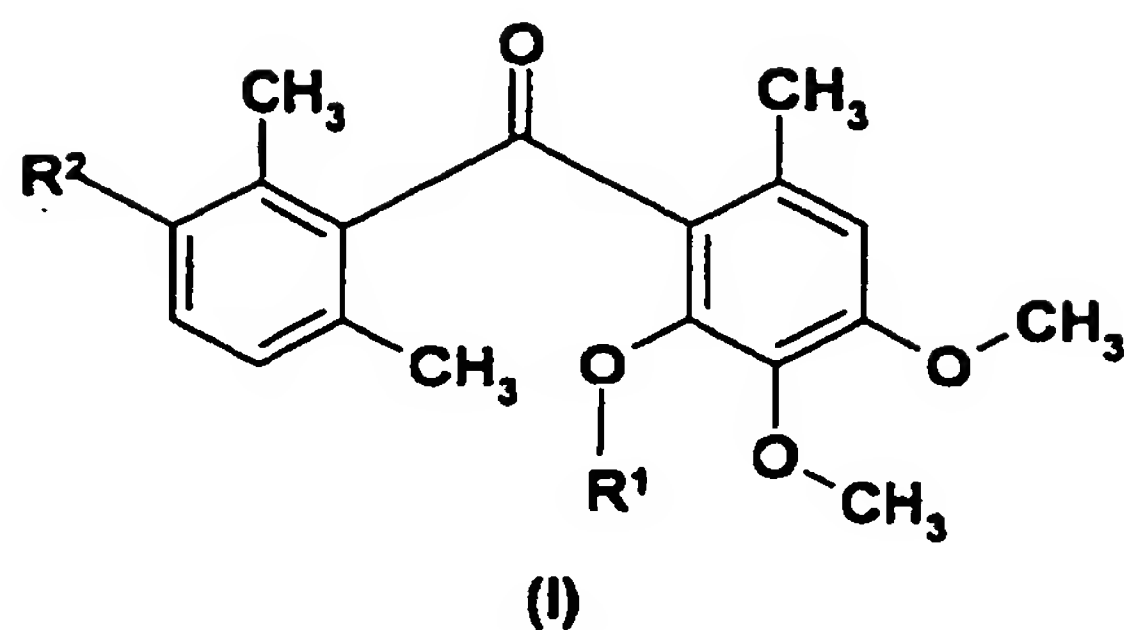
10. Verfahren zur Bekämpfung von Pilzen an einem Ort, bei dem man den Ort mit einer Verbindung nach Anspruch 3 oder Anspruch 6 oder einer Zusammensetzung nach Anspruch 9 behandelt.

11. Verfahren nach Anspruch 10, bei dem die Krankheit durch Ascomyceten verursacht wird.

12. Verfahren nach Anspruch 10, wobei es sich bei dem Pilz um ein Mitglied aus der taxonomischen Ordnung Erysiphales handelt.

Revendications

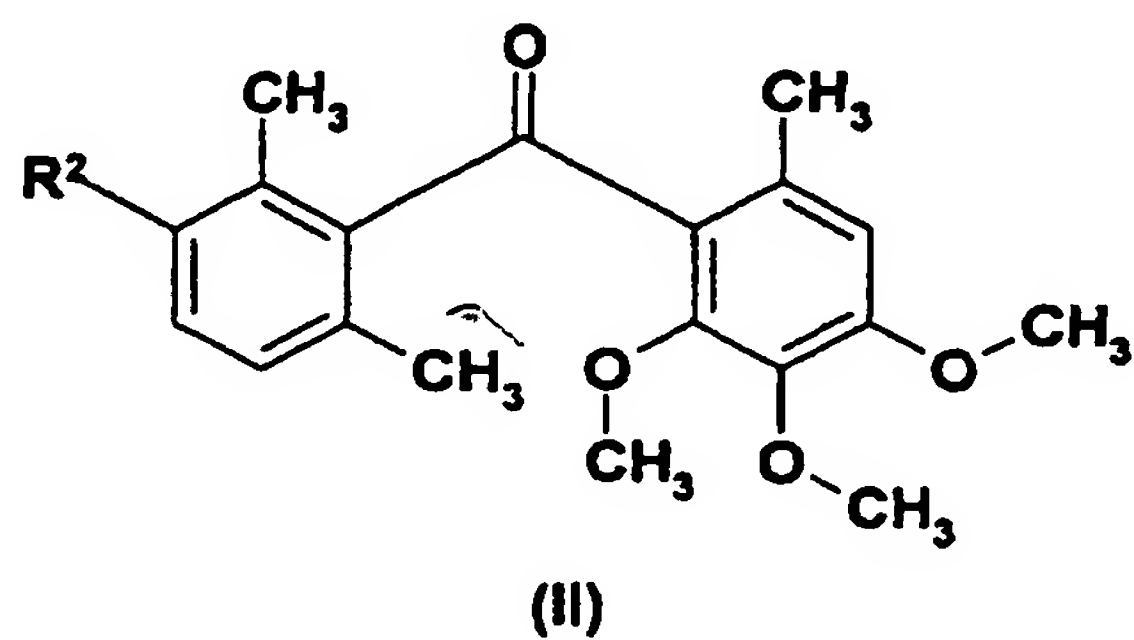
1. Procédé pour la préparation d'un composé de formule I.



dans laquelle

R¹ représente un groupe alkyle en C₂ à C₆, benzyle, cyclohexylméthyle ou alcényle en C₃ à C₆, éventuellement substitué, et

R² représente un atome d'hydrogène ou d'halogène, ou un groupe alcoxy éventuellement substitué ou un groupe nitro, qui comprend la réaction d'un composé de formule II,



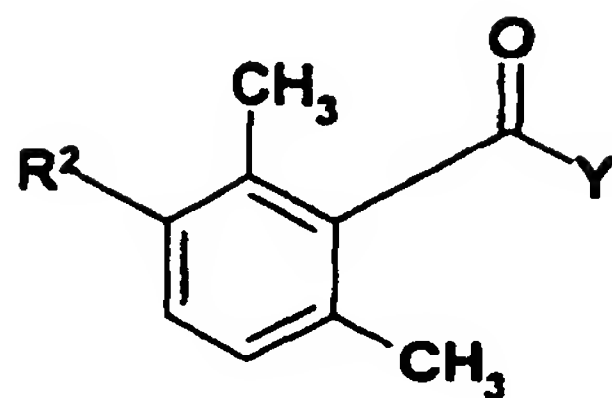
avec un composé de formule III,



dans laquelle R¹ et R² prennent la signification telle que décrite ci-dessus, et Met désigne un atome de métal alcalin.

2. Procédé pour la préparation d'un composé de formule I tel que décrit selon la revendication 1, qui comprend les étapes consistant à:

(a) faire réagir un composé de formule IV,



(IV)

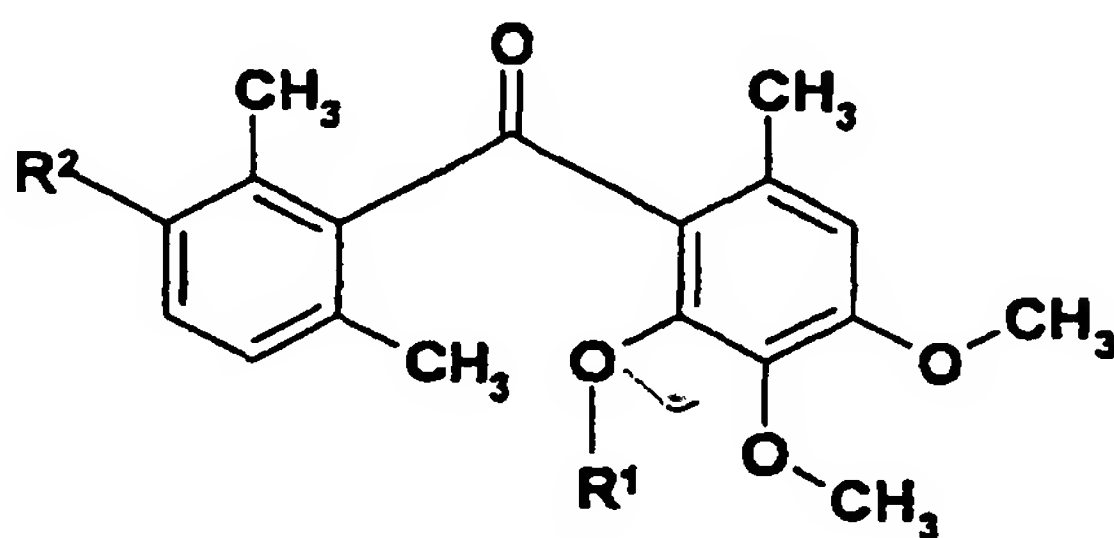
dans laquelle R^2 est tel que décrit selon la revendication 1, et Y représente un atome d'halogène ou un groupe hydroxy, avec le 3,4,5-triméthoxytoluène en présence d'un acide de Lewis ou du pentoxyde de phosphore; et (b) à traiter la benzophénone résultante par un composé de formule III,



(III)

dans lequel R^1 est tel que décrit selon la revendication 1 et Met désigne un atome de métal alcalin.

3. Composé de formule IA :



(IA)

dans laquelle

R^1 représente un groupe alkyle en C_2 à C_6 , benzyle, cyclohexylméthyle ou alcényle en C_3 à C_6 , éventuellement substitué, et

R^2 représente un atome d'halogène, ou un groupe alcoxy éventuellement substitué ou un groupe nitro.

4. Composé selon la revendication 3, dans lequel

R^1 représente un groupe alkyle en C_2 à C_5 ou benzyle, étant éventuellement substitué par un ou deux atomes d'halogène, ou un groupe alkyle en C_1 à C_3 ;

R^2 représente un atome de chlore ou de brome, ou un groupe méthoxy ou groupe nitro.

5. Composé selon la revendication 4, étant choisi dans le groupe formé par

la 3-bromo-2'-butyloxy-3',4'-diméthoxy-2,6,6'-triméthylbenzophénone,

la 2'-butyloxy-3-chloro-3',4'-diméthoxy-2,6,6'-triméthylbenzophénone,

la 2'-butyloxy-3',4'-diméthoxy-3-nitro-2,6,6'-triméthylbenzophénone,

la 2'-butyloxy-3,3',4'-triméthoxy-2,6,6'-triméthylbenzophénone,

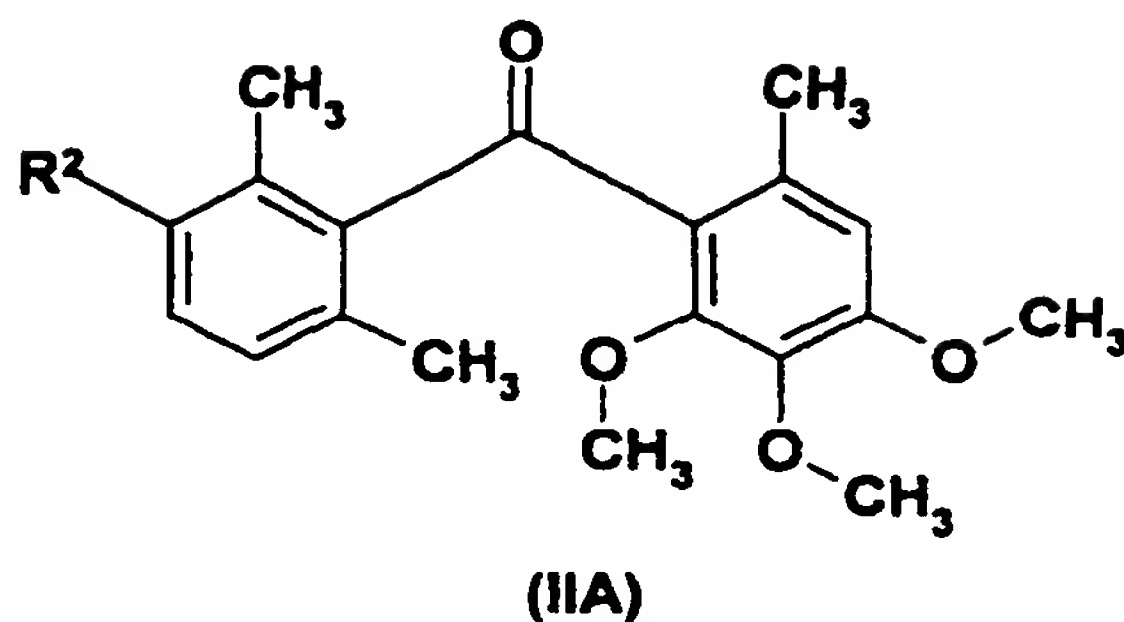
la 3-bromo-3',4'-diméthoxy-2'-(2-fluorobenzoyloxy)-2,6,6'-triméthylbenzophénone,

la 3-chloro-3',4'-diméthoxy-2'-(2-fluorobenzoyloxy)-2,6,6'-triméthylbenzophénone,

la 3',4'-diméthoxy-2'-(2-fluorobenzoyloxy)-3-nitro-2,6,6'-triméthylbenzophénone,

la 2'-(2-fluorobenzoyloxy)-3,3',4'-triméthoxy-2,6,6'-triméthylbenzophénone.

6. Composé de formule IIA :



dans laquelle

R^2 représente un atome d'halogène, ou un groupe alcoxy éventuellement substitué, ou un groupe nitro.

7. Composé selon la revendication 6, dans lequel

R^2 représente un atome de chlore ou un atome de brome ou un groupe méthoxy ou un groupe nitro.

8. Composé selon la revendication 7, étant choisi dans le groupe formé par :

la 3-bromo-2'-3',4'-triméthoxy-2,6,6'-triméthylbenzophénone,
la 3-chloro-2'-3',4'-triméthoxy-2,6,6'-triméthylbenzophénone,
la 3-nitro-2'-3',4'-triméthoxy-2,6,6'-triméthylbenzophénone, et
la 2',3,3',4'-tétraméthoxy-2,6,6'-triméthylbenzophénone.

9. Composition qui comprend une quantité efficace en tant que fongicide d'au moins un composé selon la revendication 3 ou la revendication 6 et un véhicule.

10. Procédé de lutte contre un champignon en un lieu, qui comprend le traitement du lieu par un composé selon la revendication 3 ou la revendication 6 ou par une composition selon la revendication 9.

11. Procédé selon la revendication 10, dans lequel la maladie est provoquée par les ascomycètes.

12. Procédé selon la revendication 10, dans lequel le champignon fait partie de l'ordre taxonomique des érysiphales.

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